FABRICATION AND ADDRESSABLE FUNCTIONALIZATION OF VERTICALLY-ALIGNED CARBON NANOFIBERS

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Keywords: carbon nanofibers, electrically addressable functionalization

Abstract

Recent studies have shown that carbon-based materials are extremely stable substrates for biosensing applications.[1] We are exploring vertically-aligned carbon nanofibers (VACNFs) as high-stability electrode materials for biosensing arrays. In addition to having very high chemical stability, it is likely that VACNFs also have additional interesting and useful properties due to their nanoscale width. For example, the extremely high surface area that can be obtained when carbon nanofibers are grown in the "forest" geometry may amplify the electrochemical signal that indicates biological binding to their surfaces. Additionally, VACNFs can be used as individual nanoscale sensing elements because single VACNFs can be patterned by a several methods and grown in the desired locations onto microelectrodes.

VACNFs are grown by DC plasma-enhanced chemical vapor deposition using an acetylene/ammonia mixture, catalyzed by a nickel thin film on the surface. By patterning this catalyst using electron-beam lithography, it is possible to grow small bundles of VACNFs or even individual carbon nanofibers that are electrically connected to an underlying substrate. When desired, it is also possible to deposite SiO_2 onto the VACNFs substrate so that the entire underlying electrical contact system is insulated. Additionally, using a reactive ion etch process we can expose the very end of the nanofiber so that it remains accessible for electrical measurement and/or chemical functionalization (Figure 1).[2]

We are exploring methods for functionalizing VACNFs for biological recognition. We have developed a photochemical method for terminating VACNFs forests with amines. This chemistry is very similar to that shown to form stable covalent attachment of amines to diamond, where in this case the VACNF forest sample is exposed to an N-Boc protected amino alkene in the presence of UV light. After attachment of the alkene to the surface of the nanofibers, the protecting group is subsequently removed to form amine-terminated nanofibers. The amine termination is an excellent starting point for covalent attachment of a variety of biological molecules to the surface. We have further functionalized these surfaces with DNA by reacting the amine-terminated VACNFs with a heterobifunctional cross-linker sulfosuccinimidyl 4- [N-maleimidomethyl]-cyclohexane-1-carboxylate (SSMCC), terminating the VACNFs with maleimide functionality. We then react these surfaces with 5' thiol-terminated oligonucleotides, and have shown that these oligo functionalized surfaces retain their biological recognition. The oligonucleotide tethered to the surface is specific for its complement and does not bind appreciably to a mismatched strand. Additionally, the surface is stable and can be re-hybridized after stringent denaturation conditions.

Toward the goal of using individual and small bundles of VACNFs as discrete nanoscale sensing elements, we have developed chemistry that can enable the selective functionalization of closely spaced sub-micron sized VACNF bundles with different biological molecules on the same chip.[3] The patterned, electrically addressable VACNF substrate is exposed to p-nitro benzene diazonium tetrafluoroborate in the presence of surfactant. This step terminates the nanofibers with nitrophenyl moieties. We can selectively convert individual bundles of nitrophenyl terminated nanofibers to more reactive aminophenyl terminated nanofibers using an electrochemical reduction step. This step enables the addressability of the chemistry; the fiber bundles that were *not* reduced remain terminated with nitrophenyl groups. The aminophenyl terminated bundles can then be reacted with thiol-terminated DNA and

SSMCC similarly to the method described above. After this step, another nanofiber bundle on the same chip can be reduced, and reacted with a *different* sequence of DNA, and so on. This work has implications toward the fabrication of high-density VACNF biosensor arrays.

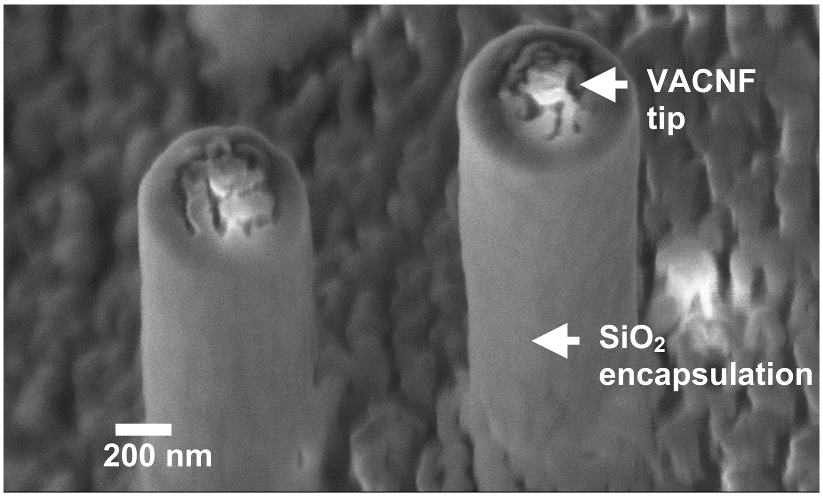

Figure 1: Electrically-addressable VACNFs with insulated sidewalls and underlying substrate, but with electrochemically active VACNF tip.

REFERENCES

1. Yang, W., et al. "DNA-modified Nancrystalline Diamond Thin Films as Stable, Biologically Active Substrates," *Nat. Mater,* 1, 253-257 (2002).
2. Guillorn, M.A. et al. "Individually Addressable Vertically-Aligned Carbon Nanofiber-based Electrochemical Probes," *J. App. Phys ,*91, 6, 3824-3828 (2002).
3. Lee, C.-S. et al. "Electrically-Addressable Biomolecular Functionalization of Carbon Nanotube and Carbon Nanofiber Electrodes," *Nanolett*, 4, 9, 1713-1716 (2004).